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Evaluation of a Denuder-MOUDI-PUF Sampling System to Measure the Size Distribution of Semi-Volatile Polycyclic Aromatic Hydrocarbons in the Atmosphere

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This study describes a field comparison conducted between 2 methods employing different MOUDI impactor configurations to evaluate their performance in sampling and measurement of the size distribution of 15 priority pollutant polycyclic aromatic hydrocarbons (PAHs). Samples were collected during 24 h periods approximately every 7th day, beginning at 8:00 AM, in 2 different sites of the Los Angeles Basin. One site was near Central Los Angeles in an area impacted by high vehicular traffic, whereas the other site was located about 60 km downwind of central Los Angeles (receptor site). Particle samples from about 43 m^3 of air were collected using collocated MOUDI impactors and classified in 3 aerodynamic diameter size intervals: 0–0.18 μm (ultrafine mode I), 0.18–2.5 μm (accumulation mode II), and 2.5–10 μm (coarse mode III). One MOUDI operated in the conventional mode, the other with a vapor trapping system that included an XAD-4 coated annular denuder placed upstream of the impactor and a polyurethane foam plug (PUF) placed in series behind the impactor. PAHs were separated and quantified by HPLC with fluorescence detection optimized for the highest sensitivity. The results showed that for both sites, using either sampling system, the size distributions obtained are similar for the less volatile PAHs (log $[p^\circ L] \leq -3.2$), but different for the more volatile PAHs (log $[p^\circ L] \geq -2.06$). In the central Los Angeles site, the largest PAH fraction was found in the 0–0.18 μm (mode I) size range, typical of primary emissions. At the downwind location, the largest fraction was in the 0.18–2.5 μm (mode II) size range, consistent with an "aged" aerosol. At both sites, albeit not statistically significant, the mean regular to denuded MOUDI mass ratios were 33–36% and 11–19% higher, respectively, for the more volatile and the less volatile PAH groups. Sampling with the regular MOUDI configuration is simpler and thus recommended for measurement of the size distribution of PAHs in either group.

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INTRODUCTION

Combustion-derived aerosol consists of a complex mixture of organic and inorganic particle- and vapor-phase compounds. Of the organic compounds associated with combustion-generated particles, polycyclic aromatic hydrocarbons (PAHs) are of particular concern because they are present in the respirable size range and several are potent mutagens and carcinogens (NAS 1983). Atmospheric PAHs may undergo homogeneous and/or heterogeneous reactions. For example, for naphthalene, the simplest and most abundant gas-phase PAH in polluted urban areas (Arey et al. 1987; Arey et al. 1989), its major atmospheric loss process is the reaction with the hydroxyl (OH) radical (Sasaki et al. 1997).

Persistent organic species are advected from their sources to downwind locations and remote areas. During transport, the atmospheric fate of PAHs is primarily governed by their chemical stability, gas-particle partitioning, and size distribution. When partitioning occurs during transport, PAH size distributions may be altered and result in changes in their dry/wet deposition

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and deposition efficiency in the human respiratory system. Size distributions of PAHs with log $[p^{\circ}L] < -2$ have been widely reported in the literature for samples collected in roadway tunnels and ambient air using cascade and low pressure impactors (Venkataraman and Friedlander 1994a; Allen et al. 1996; Schnelle et al. 1996; Miguel et al. 1998; Marr et al. 1999; Leotz-Gartziandia et al. 2000; Schnelle-Kreis et al. 2001). However, size distribution data for PAHs found predominantly in the gas phase (e.g., naphthalene, acenaphthene, fluorene, phenanthrene, and anthracene) are not available. The amounts of these semi-volatile organic compounds (SVOC) collected on impactor stages are small and evaporative losses are expected to be significant. To examine evaporative losses that occur as a result of the pressure drop within a sampling device, Zhang and McMurry (1991) developed a theoretical model, assuming that temperature, gas, and particle concentrations remain constant during sampling. This model predicts that the sampling efficiencies of particle-collecting media such as filters are always poorer than those of impactors when denuders are used upstream of these filters or impactors. According to this model, however, evaporative losses of adsorbed or absorbed SVOC species collected by impactors may be large for those that are predominantly partitioned in the gas phase.

To determine the extent of such evaporative losses during size-resolved sampling of semi-volatile and less volatile particulate PAHs, a series of field experiments were conducted in 2 of the Southern California Particle Center and Supersite (SCPCS) sampling sites located in the Los Angeles basin: Downey, near Central Los Angeles, and Rubidoux, in the inland eastern valley of the basin located about 60 km downwind of Central Los Angeles. Samples were collected using 2 colocated three-stage microorifice uniform deposit impactors (MOUDI Model 110, MSP Corp., Minneapolis, MN): one MOUDI operated in its conventional configuration, whereas the other MOUDI operated with a gas-trapping system that included an XAD-4 coated annular denuder preceding the impactor and a polyurethane foam plug (PUF) placed downstream of the impactor. The results of the size distributions of 15 of the 16 U.S. EPA "Priority Polycyclic Aromatic Hydrocarbon Pollutants" of particles collected with both sampling configurations are evaluated and presented in this paper.

EXPERIMENTAL SECTION

Sample Collection and Sites

Sampling was carried out for 24 h periods every 7th day beginning at 8:00 AM during a 4 week field campaign in Downey starting September 28, 2000, and 5 weeks in Rubidoux beginning August 23, 2001. Downey is a typical urban area near Central Los Angeles, where primarily vehicular sources and, to a lesser extent, nearby industrial activities are responsible for particulate matter (PM) emissions. Two major freeways, frequently congested with heavy-duty diesel trucks, are located within 2–4 km upwind from this site. Rubidoux is located in the inland eastern valley of the Los Angeles basin, about 60 km east of Central Los Angeles. At this downwind site, PM is primarily formed by secondary gas-to- particle reactions or by wind-blown dust from the nearby deserts (Kim et al. 2000). In addition, PM originally emitted in urban Los Angeles is advected into the Rubidoux area after several hours of atmospheric transport. In this paper we will therefore refer to the Downey air pollution regime as "source" and Rubidoux as "receptor" areas of the Los Angeles Basin (Figure 1).

Particles were deposited on Teflon filters using two colocated three-stage MOUDI impactors with 3 size intervals: 0–0.18 μm (mode I), 0.18–2.5 μm (mode II), and 2.5–10 μm (mode III) aerodynamic diameter (dp), operated at 30 LPM. These size intervals were chosen to allow quantification of the target PAHs in 24 h samples, while collecting particles in the ultrafine, accumulation, and coarse modes. An uncoated 47 mm diameter quartz fiber filter (Pallflex Corp., Putnam, CT) was used as an impaction substrate for the 10 μm cut-point stage of the MOUDI to remove particles larger than 10 μm. This substrate has been shown to minimize particle bounce when compared to impaction substrates such as aluminum or teflon (Chang et al. 1999; Chang et al. 2001). We refer to each size interval as "mode" to avoid confusion as specific terms (e.g., fine and ultrafine particles) may have different meanings between

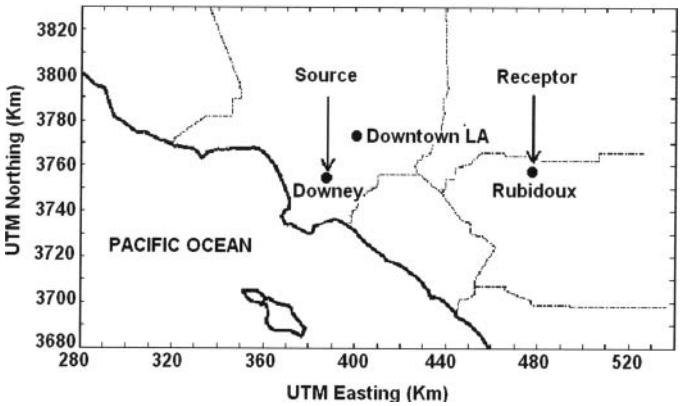

Figure 1. Source and receptor sampling sites in the Los Angles Basin.

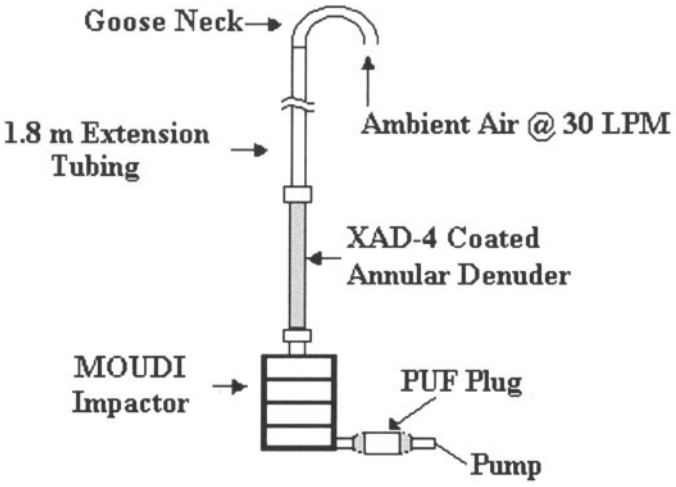

Figure 2. Schematic of the denuder-MOUDI-PUF sampling system. A three-stage regular MOUDI impactor (not shown) was used to collect parallel samples.

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disciplines and investigators. One MOUDI was operated in the "regular" mode; another impactor, referred to as "denuded" MOUDI, operated with a gas-trapping system that included an XAD-4 coated annular denuder placed upstream of the impactor and a PUF placed in series behind the impactor to capture particle-bound PAHs lost from the filter (Figure 2). A single-channel University Research Glassware (URG, Chapel Hill, NC) annular denuder 24.2 cm long, 304 cm^2 surface area (URG-2000-30B) was used in Downey and a four-channel URG denuder 50 cm long, 1,558 cm^2 surface area (URG-2000-30 × 500-4CSS) was used in Rubidoux. Collection efficiencies calculated at 30 LPM and 25°C using the Possanzini equation (Possanzini et al. 1983) were 99.6% and 80.4% for naphthalene, respectively, for the four-channel and the single-channel denuder, and 99.2% and 76.2% for benz[a]anthracene (Morris 2002). The denuders were cleaned and coated with XAD-4 following well-established procedures described in detail elsewhere (Gundel and Lane 1999; Gundel et al. 1995; Gundel 1998; Stockburger and Gundel 1999; Lewtas et al. 2001). Before use, PUF plugs were washed in tap water, rinsed well with deionized water, dried in a vacuum oven overnight at 40°C, and then compression cleaned with hexane containing 10% v/v diethyl ether.

PAH Extraction

A mixture of hexane:dichloromethane:methanol (1:1:1 v/v) was used to extract the PAHs from the denuders, which were half filled with the mixture and inverted 20 times (10 complete revolutions) with one quarter turn axial rotation for each inversion. The extract was poured out into an amber glass bottle while supporting and rotating the denuder. This procedure was repeated 4 times and all the extracts were combined. The teflon filters corresponding to each size cut were placed in amber vials with teflon-lined caps, extracted with 1.5 mL of dichloromethane (DCM) by ultrasonication for 24 min, and then filtered using 5.0 μm nylon membrane filters. The filter extracts were solvent exchanged by adding 0.1 mL of acetonitrile to a 1 mL aliquot of the DCM extract followed by volume reduction (without drying!) to ~0.1 mL by evaporation at room temperature inside an empty desiccator. The exact reduced volume was measured with a chromatographic syringe. The PUF plugs were Soxhlet extracted for 8 h with ~400 mL of hexane containing 10% v/v diethyl ether. The volumes of the PUF and the denuder extracts were reduced to ~5 mL using a rota-evaporator.

PAH Separation and Quantification

PAHs were separated using a Supelcosil LC-PAH, 15 cm, 5 μm column adapted with a Supelcosil guard column (Supelco, Bellefonte, PA). A mobile-phase solvent gradient of acetonitrile and water (40:60 over 20 min, 100:0% for another 20) was maintained at a flow rate of 0.9 mL min^{-1} using an HP 1100 HPLC series (Agilent Technologies, Delaware, USA) system consisting of a quaternary pump, a degasser, a thermostatted column compartment maintained at 25°C, and a scannable fluorescence detector. The PAH excitation and fluorescence emission conditions used (see Table 1) were previously optimized to obtain the highest sensitivity (Eiguren-Fernandez and Miguel 2002). The chromatographic time periods and fluorescence conditions used ($\lambda_{ex}/\lambda_{em}$) were NAP, ACE, and FLU (220/335) 0–14.3 min; PHE (260/360) 14.3–15.3 min; ANT (245/382) 15.3–16.3 min; FLT (235/449) 16.6–17.2 min; PYR (235/389) 17.2–19.5 min; BAA (300/410) 19.5–21.1 min; CRY (265/381) 21.1–22.5 min; BBF, BKF, and BAP (260/420) 22.5–27.5 min; DBA and BGP (295/420) 27.50–31.6 min; and IND (300/500) 31.6–40.0 min. The system was calibrated using a Radian (Austin, TX) 16 priority PAH standard (ERS-010, 10 μg mL^{-1} in acetonitrile) diluted with HPLC-grade acetonitrile to produce individual standards of 5–250 pg uL^{-1}. SRM 1649a was used as a positive control. PAH amounts found in the blanks (teflon filters and PUF plug) were subtracted from the sample values,

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Table 1
PAH codes, molecular weight, subcooled liquid vapor pressure at 293°K, and HPLC-FL instrument detection limits

PAH	Code	MW	(log $p^{\circ}L$)[a]	IDL[b] (pg)
Naphthalene	NAP	128	1.59	0.52
Acenaphthene	ACE	154	0.18	0.16
Fluorene	FLU	166	−0.15	1.18
Phenanthrene	PHE	178	−0.95	0.72
Anthracene	ANT	178	−1.11	0.31
Pyrene	PYR	202	−1.92	0.47
Fluoranthene	FLT	202	−2.06	1.29
Benz[*a*]anthracene	BAA	228	−3.22	1.04
Chrysene	CRY	228	−3.97	0.37
Benzo[*ghi*]perylene	BGP	276	−4.65	2.25
Benzo[*a*]pyrene	BAP	252	−4.67	0.75
Benzo[*b*]fluoranthene	BBF	252	−4.99	1.09
Benzo[*k*]fluoranthene	BKF	252	−5.39	0.32
Dibenz[*a,h*]anthracene	DBA	278	−7.04	1.32
Indeno[*1,2,3-cd*]pyrene	IND	276	[c]	18.5

[a]Data from Peters et al. (2000).
[b]Instrument Detection Limit.
[c]Not available.

thus defining the limit of detection of the analytical protocol. The instrument detection limit (IDL) at an S/N ratio = 5 for a 20 μL injection of the 15 PAHs ranged from 0.16 to 18 pg (Table 1). Method standard deviations for the 15 target PAHs running triplicate analysis of the positive control standard (SRM 1649a) averaged 8.0% and ranged from 3.8 to 15%. Correlation coefficients $r^2 \geq 0.999$ were obtained with five-point calibration injections in the range of the expected PAH concentrations.

RESULTS AND DISCUSSION

PUF and Denuder Measurements

The main purpose of this study was to examine the extent of evaporative losses during size-resolved sampling of semi-volatile PAHs. It was not intended to be an evaluation of the partitioning phenomena that govern the atmospheric behavior of PAHs. For detailed descriptions of the processes that occur with a range of SVOCs, the reader is referred to articles in the open literature and references therein (Junge 1977; Gustafson and Dickhut 1994; Pankow 1987, 1994; Cotham and Bidleman 1995; Liang et al. 1997; Mader and Pankow 2001; Lohmann et al. 2000).

Mean PAH concentrations measured at both sites in the PUF and the denuder are shown in Table 2, along with concentrations measured in the teflon filters. For the more volatile PAH group (NAP-FLT), the mass collected in the PUF represents 39 and 12% of the total mass, respectively, in Downey (single-channel denuder) and Rubidoux (four-channel denuder). For this reason, with the sampling parameters used and the prevailing ambient conditions, defining the particle-bound fraction of any semi-volatile PAH as the sum of the MOUDI and PUF masses to the total would clearly overestimate the particle-phase

Table 2
Mean PAH concentrations measured in the denuder, teflon filters, and PUF at the source (Downey) and the receptor site (Rubidoux)

	Downey, pg m^{-3}				Rubidoux, pg m^{-3}			
PAH	Denuder[a]	PUF	TFd	TFr	Denuder[b]	PUF	TFd	TFr
NAP	3.26E + 04	1.98E + 04	60.5	84.1	5.95E + 03	2.96E + 03	26.4	42.2
ACE	1.82E + 03	6.96E + 02	13.3	14.6	1.61E + 04	3.07E + 02	<LOD	0.4
FLU	4.08E + 03	5.58E + 03	580	608	1.93E + 04	1.61E + 03	<LOD	1.2
PHE	6.57E + 03	4.15E + 03	57.0	78.7	7.83E + 03	1.39E + 02	25.2	28.3
ANT	4.79E + 02	4.39E + 02	11.5	17.8	1.74E + 02	3.60E + 02	7.84	3.4
PYR	1.93E + 03	1.86E + 02	167	266	1.73E + 03	1.80E + 03	30.5	37.4
FLT	9.05E + 02	1.99E + 02	37.0	60.1	1.28E + 03	2.59E + 02	11.0	16.0
BAA	30.5	<LOD	62.5	88.4	11.8	522	15.2	12.9
CRY	85.0	212	88	131	201	443	20.3	23.5
BGP	23.0	<LOD	596	708	<LOD	5.04	104	119
BAP	12.1	<LOD	175	219	<LOD	14.6	28.0	32.1
BBF	14.7	31.1	102	138	31.8	229	31.9	39.4
BKF	6.90	<LOD	51.5	63.2	<LOD	91.7	17.0	18.0
DBA	<LOD	<LOD	19.3	24.0	<LOD	<LOD	7.29	8.79
IND	26.1	<LOD	129	150	<LOD	15.9	47.0	50.0

[a]Single-channel.
[b]Four-channel.
TFd = teflon filters, 3 MOUDI stages, denuded MOUDI. TFr = teflon filters, 3 MOUDI stages, regular MOUDI. <LOD = less than limit of detection.

Table 3
Measured regular MOUDI/denuded MOUDI mass ratios for each PAH mode and group and three-mode means at the source (Downey) and the receptor site (Rubidoux)

	Downey				Rubidoux			
PAH group	Mode I	Mode II	Mode III	3-Mode mean	Mode I	Mode II	Mode III	3-Mode mean
NAP-FLT[a]	1.26	1.61	1.21	1.36	1.17	1.84	0.99	1.33
BAA-IND[b]	1.31	1.11	1.14	1.19	0.66	1.52	1.15	1.11

PAH group: [a]$\log [p^{\circ}L] \geq -2.06$; [b]$\log [p^{\circ}L] \leq -3.22$.

concentration. For PAHs in the less volatile group (BAA-IND) the results are mixed; with the single-channel denuder, part of the CRY and all of the BBF mass found in the PUF may be used to calculate the particle-bound fraction. With the four-channel denuder, the mass found in the PUF may be used to calculate the particle-bound fraction of BGP, BAP, and IND, but not of BAA, CRY, BBF, and BKF as these PAHs clearly escaped capture by the denuder (Table 2). Although the five-fold larger surface area of the four-channel denuder markedly improved the collection efficiency of PAHs in the more volatile group, the actual efficiency observed with this denuder is much lower than estimated using the Possanzini equation (Morris 2002).

Regular versus Denuded MOUDI Mass Ratios

Measured regular MOUDI/denuded MOUDI mass ratios for each PAH mode and group, and the three-mode means for the source (Downey) and the receptor site (Rubidoux), are shown in Table 3. At both sites, the mean regular to denuded MOUDI mass ratios were higher for both PAH groups. For the less volatile PAH group (BAA-IND), the largest ratio (1.31) was found in mode I in the source area and in mode II in the receptor area (1.52). These modes had the highest PAH mass fraction (see Figure 4) for this group. For the more volatile PAH group (NAP-FLT), the largest mass ratios were found in mode II, respectively, at the source (1.61) and receptor site (1.84). However, neither mode contained the highest mass fraction. The more volatile PAH group had the largest 3-mode means, respectively, 1.36 and 1.33, for the source and receptor site. The observed higher mass ratio for the more volatile PAHs is consistent with higher desorption losses from the denuded MOUDI. If the Kelvin effect were the only operating mechanism responsible for mass losses, it would enhance desorption from the smallest particles and give a higher mode I mass ratio. The observed mass ratios (Table 3) suggest that a combination of mechanisms may be operating at both sites. Chemical reactions that may contribute to loss of PAH mass are discussed below.

Mean PAH concentrations, defined as the sum of the individual concentrations measured in the teflon filter of each of the 3 stages, with the regular MOUDI and the denuder-MOUDI-PUF samplers are shown in Figure 3. Except for FLU, the PAH profiles observed at the source and receptor sites are similar. Albeit not statistically significant, at both sites mean concentrations obtained with the regular MOUDI were consistently higher than with the denuded MOUDI (Figure 3). Chemical reactions may contribute to decreased concentrations of particle bound PAHs during transport. The atmospheric lifetimes (2.9–11 h) calculated by Arey (1998) for day time gas-phase reactions of OH with target PAHs in the more volatile group are smaller than the observed fine particle transport time (15–25 h) from the Central Los Angeles area to the receptor area (Pandis et al. 1992), thus allowing time for reactions to occur during transport. The atmospheric lifetimes for nighttime gas-phase reactions of NO_3 with these PAHs range from days to years (Arey 1998), except for ACE (1.2 h) and PHE (4.6 h). For heterogeneous reactions, Kamens et al. (1988) showed evidence of and quantified the photolysis of PAHs on atmospheric soot particles with respect to humidity, sunlight, and temperature. In addition to dilution, dry/wet deposition, and partitioning, these reaction mechanisms may have contributed to the observed PAH losses during atmospheric transport. The faster disappearance of particle-bound FLU, found in high concentrations in the source area but near the LOD at the downwind site (see Figure 3), suggests that its heterogeneous reaction is relatively faster than that for other PAHs in the more volatile group.

Except for ANT and BAA in the Rubidoux samples, sampling with the regular MOUDI configuration resulted in consistently higher total concentrations. Two distinct mechanisms may explain this finding. First, sampling with a regular MOUDI may lead to higher PAH concentrations due to some sorption of vapor-phase PAHs on the collected particles and matrix (a positive artifact). On the other hand, with the denuded MOUDI configuration, when the air exits the denuder the system is no longer under thermodynamic equilibrium. In this case, the expected result would be some desorption of PAHs from the impactor filters and substrates (a negative artifact). We believe that the latter mechanism is more likely to have occurred than the former for the following reasons. First, adsorption of vapor and gas-phase compounds on impactor stages is substantially hindered by the stagnation boundary layer formed in the impaction zone (Zhang and McMurry 1991; Chang et al. 1999). Furthermore, the use of teflon filters as particle collection media in the MOUDI stages should make adsorption of organic vapors

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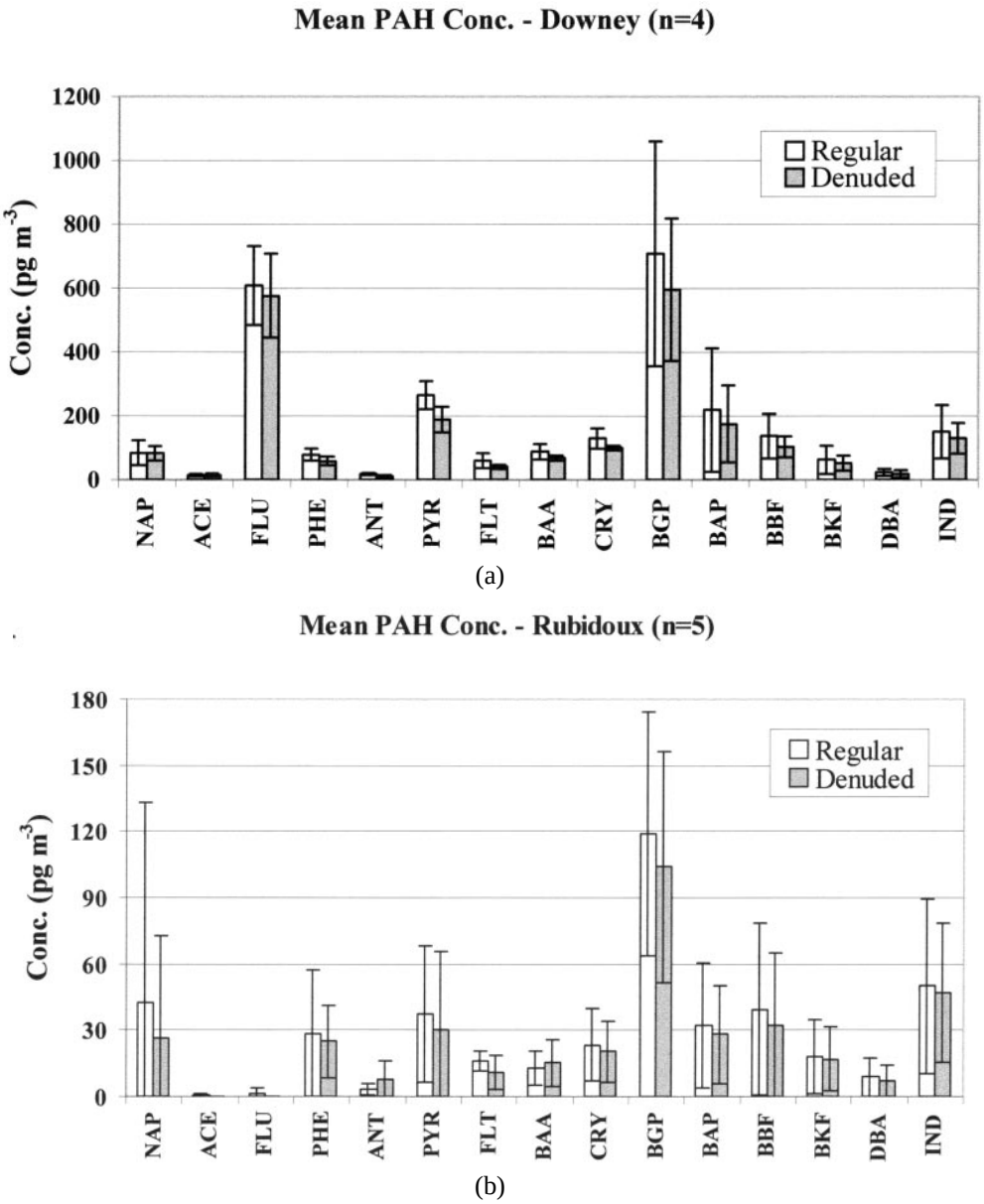

Figure 3. Comparison of PAH concentrations measured with the regular MOUDI impactor and with the denuder MOUDI-PUF system in the source site (a) and the receptor site (b). For each PAH, the concentration indicated represents the sum of the concentration means (± SDEV) measured with each sampling system. For the source samples, the sum of the PAH concentrations was 2,649 pg m^{-3} and 2,150 pg m^{-3}, respectively, for the regular and the denuded MOUDI configurations. For the receptor site samples, they were, respectively, 433 pg m^{-3} and 371 pg m^{-3}. All samples were corrected for filter blank.

less likely to occur when compared to media such as quartz filters that have been traditionally associated with such adsorption phenomena (McMurry and Zhang 1989). In addition, for particles of size 0.05–0.1 μm there is a potential 10% loss to the denuder tube surfaces (Peters et al. 2000), which would also contribute to a negative artifact. If diffusional wall losses were significant, we would expect them to be larger with the four-channel denuder tube. Our mass ratio data suggest that losses to the four-channel denuder tube surfaces are not significant.

PAH Size Distributions

The results of the PAH size distributions measured at the 2 sites, using the regular and the denuded MOUDI configurations, are shown in Figure 4. A few striking differences can be observed between the size distributions obtained with the regular MOUDI at Downey (source site) and Rubidoux (downwind receptor site). At the source site, with only one exception (FLU), the measured PAHs are mostly associated with mode I particles (size range 0–0.18 μm, Figure 4a). These distributions are

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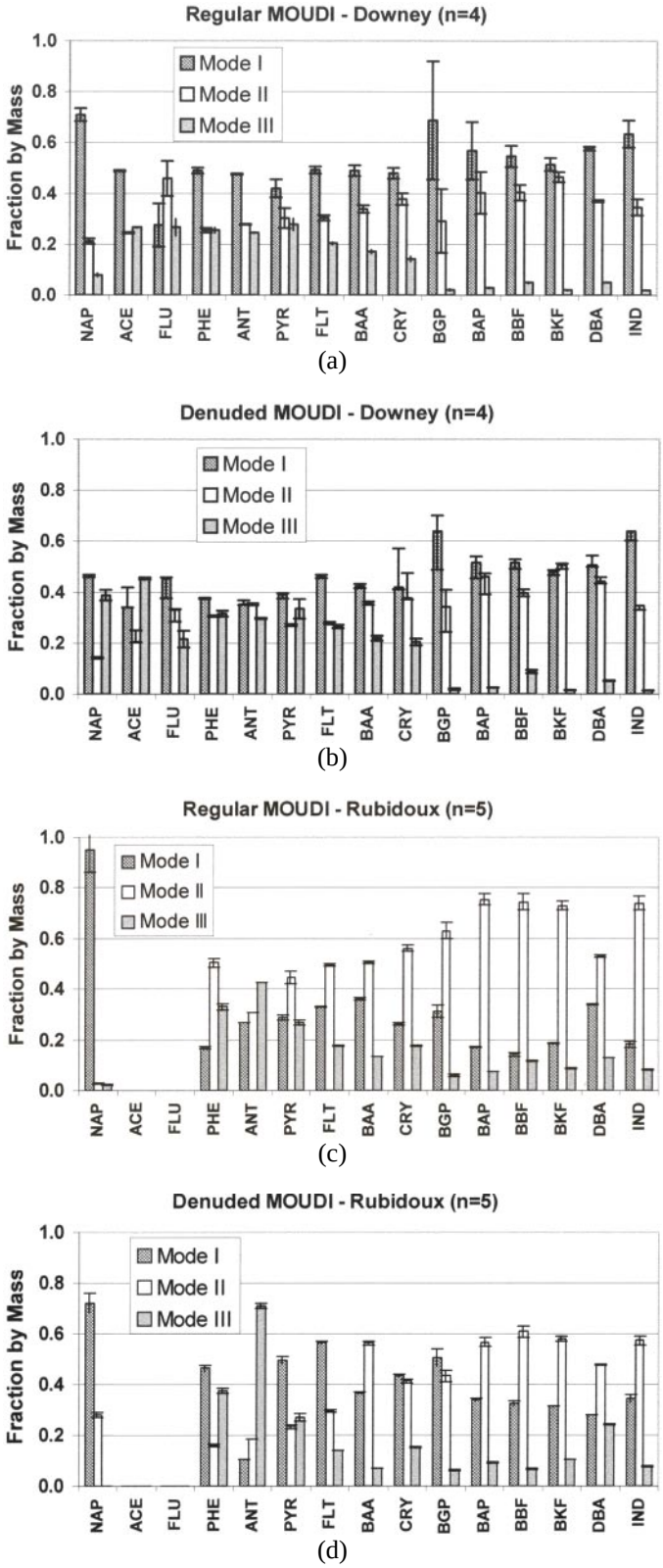

Figure 4. Particle size distributions of PAHs measured at the source and the receptor sites using the regular MOUDI (a and c) and the denuder MOUDI-PUF sampling system (b and d). Each mode corresponds to particles with aerodynamic diameters of 0–0.18 μm (mode I), 0.18–2.5 μm (mode II), and 2.5–10 μm (mode III). ACE and FLU were below the limit of detection at the receptor site. The measured regular/denuded MOUDI mass ratios for each mode and group, and the three-mode means, are shown in Table 3. All samples were corrected for filter blank.

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similar to PAH distributions measured at the Sepulveda tunnel in Central Los Angeles (Venkataraman et al. 1994) and the Caldecott tunnel, located east of Berkeley, CA (Miguel et al. 1998; Marr et al. 1999; Venkataraman et al. 1994), and are consistent with the fact that the Central Los Angeles area is strongly impacted by fresh vehicular emissions (Venkataraman and Friedlander 1994b). By contrast, in Rubidoux, except for NAP and ANT, the PAH peaks (Figure 4c) are associated with mode II particles ($0.18 < dp < 2.5$ um). Vehicular emissions in the Rubidoux area are not negligible, but are much smaller compared to those generated by light- and heavy-duty vehicles near Central Los Angeles. Except for FLU, the particle-bound PAH concentrations measured in the teflon filters in the receptor site (Rubidoux) were, on average, about 6 times smaller than those measure at Downey. Similar results for particle-phase PAHs were reported by Fraser et al. (1998) for samples collected in urban sites of the Los Angeles basin.

Previous studies conducted nearby in Riverside ($\sim$6 km southeast of Rubidoux) have shown that the fine PM fraction consists mainly of particles generated by atmospheric reactions as well as those that reach this area and were originally emitted in much higher concentrations in the Central Los Angeles area (Pandis et al. 1992; Kim et al. 2002; Singh et al. 2001). By the time they reach the Riverside area, after a period on the order of 15–25 h (Pandis et al. 1992), the particles in the air parcel agglomerate to form more stable accumulation mode particles. Allen et al. (1996) reported that in rural samples collected in Massachusetts, low and high MW PAHs were associated with both the fine and coarse aerosols and attributed to slow mass transfer by vaporization and condensation. Venkataraman et al. (1999) developed a similar adsorption model and attributed the predominance of semi-volatile PAHs in the accumulation mode to their volatilization from ultrafine particles (Kelvin effect) and subsequent partitioning to the accumulation mode where secondary organic aerosol constituents are available.

For PAHs with ($\log[p^{\circ}L] < -3$), except for CRY and BGP in Rubidoux, the size distributions obtained with or without a denuder upstream of the MOUDI were similar (Figures 4a–d). For the relatively more volatile PAHs some differences were observed. At Downey, except for FLU, the fraction of PAH mass associated with mode I particles was higher for samples collected with the regular MOUDI (Figures 4a and 4b). The observation that the denuded MOUDI at this site may underestimate the fraction of the more volatile PAHs associated with mode I particles may be attributable to a higher degree of desorption occurring in that impactor stage due to its largest pressure drop in comparison to the preceding MOUDI stages. This is also consistent with the predictions of the Zhang-McMurry model (1991) for SVOC that are predominantly in the vapor phase. For the samples collected at the downwind location with the regular MOUDI (Figure 4c), PHE, PYR, and FLT were associated with mode II particles, but, with the denuded MOUDI configuration, these PAHs were found in mode I (Figure 4d). The reason for this behavior is rather unclear. At both sampling sites, with either sampling configuration, the PAH fraction in mode III increases with increasing PAH vapor pressure. This behavior may result from the dissolution of vapor-phase PAHs into oily droplets generally found in mode III particles (Miguel et al. 1998). The observed size distributions reported in this study using the regular MOUDI configuration are consistent with the distributions measured by other researchers at 2 central Los Angeles sites (North Main St. and Pico Rivera) and at a downwind site (Upland) using a low pressure impactor (Venkataraman and Friedlander 1994a).

SUMMARY AND CONCLUSIONS

We have examined the effects of a denuder placed upstream of a MOUDI impactor on the size distributions of 15 priority pollutant PAHs, including both semi-volatile and particle-bound species, collected near Central LA and at a downwind location. Consistent with literature data, the percentage of PAHs found in the particle phase increases with decreasing vapor pressure. The use of a denuder upstream of a MOUDI does not significantly affect the size distribution shape and form of the less volatile PAHs ($\log[p^{\circ}L]) < -3$. The fraction of PAH mass in the coarse mode increased with increasing PAH vapor pressure. The strongest effect of the denuder on the size distribution was seen for the more volatile PAHs collected at the downwind site. PAH size distributions measured with either configuration peaked in the 0–0.18 μm size range (mode I) in samples collected in central Los Angeles and in the 0.18–2.5 μm size range (mode II) at the downwind receptor site. At both sites, albeit not statistically significant, the mean regular to denuded MOUDI mass ratios were higher 33–36% and 11–19%, respectively, for the semi-volatile and the less volatile PAH groups. We believe that this difference may be due to a negative artifact with the denuded MOUDI configuration. In either case, the total PAH mass differences are not statistically significant when considering chemical analysis and sampling errors. Sampling with the regular MOUDI configuration is much simpler and thus recommended to measure the size distribution of PAHs in either group.

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